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RESEARCH ON THE DYNAMIC STRUCTURE OF
LIQUIDS, LIQUID CRYSTALS AND DISORDERED
SOLIDS. RESEARCH ON SEMICONDUCTOR
MATERIALS AND DEVICES

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TECHNICAL REPORT

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Liquid Crystals and Disordered Solids
Research on Semiconductor Materials and Devices

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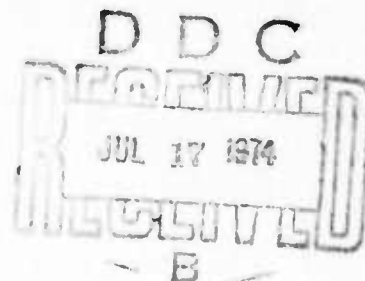
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13. ABSTRACT <p>The dynamic structure of liquids and disordered solids is investigated by Rayleigh, Brillouin and Raman light scattering, by nuclear magnetic resonance and by infrared absorption. Simple liquids, liquid crystals, polymers, glasses, organic semiconductor and hydrogen in metals are the objects of investigation.</p> <p>The properties of light emitting and laser diodes of the semiconductors GaAsP, InGaAs, and InGaP are investigated to improve and extend their behavior. Impurities and imperfections in silicon which affect the properties of solid state devices are investigated for the purpose of controlling and improving device performance.</p>			

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KEY WORDS

Liquids
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Silicon

TECHNICAL SUMMARY

I. Research on Semiconductor Materials

A. Properties of Recombination Centers in Semiconductors (C. T. Sah)

1. Technical Problems

The control of imperfections and impurities during manufacture and processing of silicon semiconductor devices is of central importance for solid state technology.

2. General Methodology

A novel capacitance technique is used to characterize imperfection centers that are electron and hole traps in silicon.

3. Technical Results

Double donor centers produced during high temperature processing have been shown to be due to abnormal concentrations of boron and phosphorus in surface layers.

4. Implications for Further Research

Double donor centers due to sulfur, zinc, and transition metal impurities should be characterized. Isovalent centers due to Group IV impurities should be examined for beneficial effects on device operation.

5. Special Comments

The capacitance technique has been adopted and extended by the Bell Telephone Laboratories during the past year.

B. Luminescence, Lasers, Carrier and Impurity Effects in Compound Semiconductors (N. Holonyak, Jr.)

1. Technical Problems

Light emitting diodes and lasers are of importance for electronic display devices and communication. Current needs are to improve efficiency, extend emission to shorter wavelengths, and develop laser capabilities.

2. General Methodology

Crystals and epitaxial layers are grown, junctions prepared by diffusion, electrical and optical properties measured in ternary III-IV compounds.

3. Technical Results

The superiority of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ over GaP:N for general light emitting devices was established and the effect of zinc impurity determined. Lasers were operated by electron beam pumping. Major progress was made in the development of $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$.

4. Implications for Further Research

Experiments are needed to explore the effect of composition on light emission and laser action of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$. The effect of N on $\text{In}_{1-x}\text{Ga}_x\text{P}$ and $\text{In}_x\text{Ga}_{1-x}\text{As}$ and improved methods of introducing Zn impurity for emitters and lasers in the orange-green region of the spectrum should be explored. Heterojunctions for optoelectronic devices should be developed in these materials.

5. Special Comments

The research is performed in collaboration with M. G. Craford of the Monsanto Company.

II. Research on the Dynamic Structure of Liquids, Liquid Crystals and Disordered Solids (W. Flygare, J. Jonas, M. Klein, W. McMillan)

1. Technical Problems

The mechanical, optical and electrical properties of liquids, amorphous solids, and polymers are of technological importance but the scientific understanding of these materials is limited by comparison with that of ordered crystals. The general objective of the research is an understanding of the dynamical structure of liquids, liquid crystals, amorphous solids and polymers.

2. General Methodology

Light scattering (Raman, Brillouin and Rayleigh) and nuclear magnetic resonance is observed with high pressure and temperature as primary variables.

3. Technical Results

The separate effects of temperature and density on the orientation and vibration of molecules of a simple liquid, methyl iodide, have been distinguished for the first time. Information concerning transfer of angular momentum has been obtained. The motional behavior of water molecules in the solvation shells of ions of electrolytes was determined. Orientational pair correlations of liquid crystal like solutions have been determined. Theories of the liquid crystal smectic C, B and H phases and a dynamical theory of the smectic A-nematic phase transition were completed. The pressure dependence of the glass transition temperature of polymers has been measured. Raman scattering from solidified noble gases, argon and krypton and from the organic crystal, TTF-TCNQ, an anomalous conductor, have been obtained.

4. Implications for Further Research

Many critical experiments begun during the past year are incomplete. These experiments include light scattering from hydrogen in niobium, from glasses, and from inorganic conducting salts. Studies of binary liquids (including metals) molten salts and β alumina type crystals appear feasible.

Light and x-ray experiments to test the theory of the smectic A-nematic liquid crystal phase transition are in progress. The preliminary polymer studies encourage experiments on the motion of carbon atoms within a chain, on chain motion, and on mobility of plasticizers.

Work on simple liquids and electrolytes should be extended to higher temperature and pressure with particular interest attached to supercritical dense water at temperatures near 1000°C and pressures of several kilobars where its electrical conductivity is similar to that of fused salts. The relationship between rotational correlations and shear viscosity near the critical point should be determined.

More information should be obtained concerning the relationship between molecular vibrations, phase transitions, and anomalous electrical conductivity of organic paraconductors.

5. Special Comments

This research is an interdisciplinary program of faculty members from the Departments of Chemistry and Physics with the cooperation of Professor Howard Birnbaum of Metallurgy on the studies of hydrogen in niobium.

SUBPROJECT REPORTS

Luminescence, Lasers, Carrier and Impurity Effects in Compound Semiconductors

Principal Investigator: Nick Holonyak, Jr., Ph.D.
Professor of Electrical Engineering

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Nick Holonyak, Jr., Professor
Joe C. Campbell, IBM Postdoctoral Fellow

Junior Staff: W. R. Hitchens, Research Assistant
Michael H. Lee, Research Assistant
M. J. Ludowise, Research Assistant
J. J. Coleman, Research Assistant, NSF
R. J. Nelson, Research Assistant, NSF

Objectives: Study III-V compounds, isoelectronic traps and complexes, spontaneous and stimulated recombination, luminescence, lasers, p-n junctions, and heterojunctions.

Approach: Crystal growth and junction formation by vapor transport, growth from solution (constant-temperature liquid-phase epitaxy [CT-LPE]), and impurity diffusion. Electrical and optical measurements (4.2-300°K) on thin homogeneous samples and on p-n junctions.

Progress: (01 07 73 - 30 06 74) Extensive work on nitrogen-doped $\text{GaAs}_{1-x}\text{P}_x$ and on CT-LPE $\text{In}_{1-x}\text{Ga}_x\text{P}$ has been carried out. With Verdeyen's group (EE) we have shown that $x = 0.47$ $\text{GaAs}_{1-x}\text{P}_x$:N can be pumped with an electron beam generated by a gas plasma and can be operated as a laser on the A-line recombination transition. If the N-doped layer is removed from the sample, the crystal proves to be indirect in its behavior. The effect of the Zn acceptor in direct and indirect $\text{GaAs}_{1-x}\text{P}_x$:N has been determined experimentally and theoretically. Beyond the direct-indirect transition, holes bound to the Zn acceptor are not involved in recombination with electrons bound

to the N (or NN) isoelectronic trap because of insufficient overlap of the electron and hole wave functions. The effect of decreasing of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ crystal composition below $x = 1$ and thus the increase of the $k = 0$ wave function component of the electron bound to the N trap has been determined and shows that an optimum LED can be approached in the crystal composition range 0.6-0.8. That is, for a comparable state of the crystal and junction art for GaP:N and $\text{GaAs}_{1-x}\text{P}_x\text{:N}$, GaP does not prove to be the right choice for a general purpose LED. The ternary exceeds the performance of the binary, as has been verified theoretically in this project and experimentally by Craford and co-workers (Monsanto). In addition to the above work, we have measured in $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ and $\text{In}_{1-x}\text{Ga}_x\text{P}$ the carrier lifetime in both the spontaneous and stimulated regimes as a function of recombination-radiation wavelength. A major change (decrease) in carrier lifetime is resolved in the region of stimulated emission.

Publications: (01 07 73 - 30 06 74)

R. D. Dupuis, N. Holonyak, Jr., M. H. Lee, J. C. Campbell, M. G. Craford, D. Finn, and D. L. Keune

Laser Operation of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ ($x=0.37$, 77°K) on Photopumped NN_3 Pair Transition

Applied Physics Letters 22, 369-371 (1973)

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10, and by the National Science Foundation under Grant GH-33771

J. T. Verdeyen, W. L. Johnson, B. E. Cherrington, N. Holonyak, Jr.,

J. C. Campbell, M. H. Lee, and M. G. Craford

Electron-Beam Pumped Semiconductor Laser Using a Gas Plasma Gun (GPG)

Applied Physics Letters 23, 102-103 (1973)

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10, by the National Science Foundation under Grants GH-3377

and GK-27559, and by the U. S. Army Night Vision Lab

H. M. Macksey, M. H. Lee, N. Holonyak, Jr., W. R. Hitchens, R. D. Dupuis, and J. C. Campbell

Crystal and Luminescence Properties of Constant-Temperature Liquid-Phase-Epitaxial $\text{In}_{1-x}\text{Ga}_x\text{P}$ ($x=0.7$) Grown on (100) $\text{GaAs}_{1-x}\text{P}_x$ ($x=0.4$)
Journal of Applied Physics 44, 5035-5040 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771, and by the U. S. Army Night Vision Lab

C. B. Duke and N. Holonyak, Jr.

Advances in Light Emitting Diodes. Traps and Resonance in III-V Ternary Alloys: A New Dimension in Semiconductor Light
Physics Today 26, 23 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

J. C. Campbell, N. Holonyak, Jr., M. H. Lee, M. J. Ludowise, M. G. Craford, D. Finn, and W. O. Groves

Recombination Transitions in Zn-N-Doped $\text{GaAs}_{1-x}\text{P}_x$ in the Direct and Indirect Composition Regions

Journal of Applied Physics 45, 795-799 (1974)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, and by the National Science Foundation under Grant GH-33771

N. Holonyak, Jr., J. C. Campbell, M. H. Lee, J. T. Verdeyen, W. L. Johnson, M. G. Craford, and D. Finn

Pumping of $\text{GaAs}_{1-x}\text{P}_x$:N (at 77°K, for $x \leq 0.53$) by an Electron Beam from a Gas Plasma

Journal of Applied Physics 44, 5517-5521 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grants GH-33771, GK-37759, and by the U. S. Army Night Vision Lab under Contract DAAK-02-72-C-0076

M. H. Lee, N. Holonyak, Jr., J. C. Campbell, W. O. Groves, M. G. Craford, and D. L. Keune

Spontaneous and Stimulated Carrier Lifetimes (77°K) in $\text{GaAs}_{1-x}\text{P}_x$:N
Applied Physics Letters 24, 310-313 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

J. C. Campbell, W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, M. J. Ludowise, and J. J. Coleman

Luminescence, Laser and Carrier-Lifetime Behavior of Constant-Temperature LPE $\text{In}_{1-x}\text{Ga}_x\text{P}$ ($x=0.52$) Grown on (100) GaAs
Applied Physics Letters 24, 327-330 (1974)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

M. H. Lee, N. Holonyak, Jr., J. C. Campbell, W. O. Groves, and M. G. Craford
Behavior of Above-Gap NN-Pair States in Radiative Recombination in $\text{GaAs}_{1-x}\text{P}_x\text{:N}^+$
($x=0.24$, 77°K)

Journal of Applied Physics 45, 1775-1778 (1974)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33771

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Model Calculations for Radiative Recombination in Zn-N-Doped $\text{GaAs}_{1-x}\text{P}_x$
in the Direct and Indirect Composition Region

Physical Review B (May 15) (1974)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grants GH-33634
and GH-33771, and by the Aerospace Research Lab, USAF AFB Contract
F-33615-72-C-1506

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, and J. C. Campbell
Liquid Phase Epitaxial Growth and Photoluminescence Characterization of
Laser-Quality (100) $\text{In}_{1-x}\text{Ga}_x\text{P}$

Journal of Crystal Growth (submitted to)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10

J. C. Campbell, N. Holonyak, Jr., A. B. Kunz, and M. G. Craford
Effect of Crystal Composition on "Quasi-Direct" Recombination and LED
Performance in Indirect Region of $\text{GaAs}_{1-x}\text{P}_x\text{:N}$

Applied Physics Letters 25, (1974)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grants GH-33634
and GH-33771, and the Aerospace Research Laboratory

M. H. Lee, N. Holonyak, Jr., W. R. Hitchens, J. C. Campbell, and M. Altarelli
The Direct-Indirect Transition $\text{In}_{1-x}\text{Ga}_x\text{P}$
Solid State Communications (submitted to)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771,
by the U. S. Army Night Vision Lab DAAK-02-72-C-0076, and by the U. S.
Army Research Office under Contract DAHC-04-74-C-0005

J. C. Campbell, N. Holonyak, Jr., M. G. Craford, and D. L. Keune
Band Structure Enhancement and Optimization of Radiative Recombination in
 $\text{GaAs}_{1-x}\text{P}_x\text{:N}$ (and $\text{In}_{1-x}\text{Ga}_x\text{P:N}$)

Journal of Applied Physics (submitted to)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, and by the National Science Foundation under Grant GH-33771

W. R. Hitchens, N. Holonyak, Jr., M. H. Lee, J. C. Campbell, J. J. Coleman,
W. O. Groves, and D. L. Keune

Liquid Phase Epitaxial (LPE) Grown-Junction $\text{In}_{1-x}\text{Ga}_x\text{P}$ ($x \sim 0.63$) Laser of
Wavelength $\lambda \sim 5900 \text{ \AA}$ (2.10 eV, 77°K)

Applied Physics Letters (submitted to)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grant GH-33771,
and by the U. S. Army Night Vision Lab DAAK-02-72-C-007

M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

Joe Charles Campbell (N. Holonyak, Jr. Adviser)

Indium Gallium Arsenide and Indium Phosphide Injection Lasers and Radiative
Recombination in Nitrogen-Zinc-Doped Gallium Arsenide Phosphide
October 1973

Supported by the Advanced Research Projects Agency under Contract
HC-15-67-C-0221, by the National Science Foundation under Grants GK-18960
and GH-33771, by the University Industrial Affiliates Program, Night
Vision Lab DAAK-02-73-C-0076, and by JSEP DAAB-07-67-C0199

Properties of Recombination Centers in Semiconductors

Principal Investigator: Chih-Tang Sah, Ph.D.
Professor of Electrical Engineering and of Physics

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Chih-Tang Sah, Professor
Soong H. Lee, Visiting Research Assistant Professor
Chi-Tong Wang, Visiting Research Assistant Professor
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Junior Staff: Chak Lun Chie, Research Assistant
F. Hennig, Research Assistant
Thomas Y. Lo, Research Assistant
Chyan-Chang Shiue, Research Assistant
Phillip D. Wright, Research Assistant

Objectives: (1) To obtain highly accurate energy level schemes and macroscopic capture and emission rates of electrons and holes at imperfection centers in semiconductors. (2) To develop quantum mechanical theories to interpret these fundamental parameters from atomic models. (3) To use these results to predict the electrical and optical properties of silicon diodes, transistors, integrated circuits and compound semiconductor devices.

Approach: The macroscopic transition rates and energy level schemes of bound electrons and holes are measured from current and high frequency capacitance transients in p-n junctions after switching electrically, optically, or thermally. Theoretical quantum models and analyses are developed from a two parameter impurity potential, including the central cell effect, and from first principle impurity pseudopotentials derived from published self-consistent atomic potentials.

Progress: (01 07 73 - 30 06 74) The highly sensitive (better than 10^{11} centers per cm^3) depletion layer capacitance transient technique has been used to determine the origin of the double donor quench-in centers in silicon after high temperature processing. Results of extensive sets of experiments are designed in which the concentration of phosphorus and boron in the diffused layer, the diffusion temperature and times are varied. These experiments show that the centers are definitely associated with the presence of very high concentrations of surface layers of boron and phosphorus. It is also shown that these centers have very high diffusion coefficients and a formation energy of 2.2 eV. These results are consistent with the vacancy model proposed by us previously. Properties of Cr centers in silicon are also investigated using the capacitance transient on Schottky barriers made on chromium doped silicon. The junction capacitance method has also been used to determine the low-electric-field and thermal equilibrium values of the thermal capture and emission rates of electrons and holes at the gold donor and acceptor centers in silicon. Very high resistivity silicon is employed (1 to 10 K ohm-cm). New and reliable temperature and electric-field dependences of these rates are obtained and the temperature dependence of the thermal activation energy or energy level of these centers from the band edges are obtained. The mass action law has been verified to within a factor of two. Interfacing equipment has been built and assembled to provide online analysis of experimental data and successful operation has been achieved.

Publications: (01 07 73 - 30 06 74)

D. H. Eaton and C. T. Sah

Series Equivalent Circuit Representation of SiO_2 -Si Interface and Oxide Trap States

Solid State Electronics 16, 841-846 (1973)

Supported by the National Science Foundation under Grants GH-33634 and GK-30283, by the Advanced Research Projects Agency under Contract HC-15-67-0221, and by AFOSR-71-2067

J. M. Herman III and C. T. Sah

Thermal Capture of Electrons and Holes at Zinc Centers in Silicon

Solid State Electronics 16, 1133-1139 (1973)

Supported by the National Science Foundation under Grant GH-33634, by the Advanced Research Projects Agency under Contract HC-15-67-C-0221, and by AFOSR-71-2067

K. Hess and C. T. Sah

Hot Carriers in Silicon Surface Inversion Layers

Journal of Applied Physics 45, 1254-1257 (1974)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by AFOSR-71-2067

M. J. McNutt and C. T. Sah

High Frequency Space Charge Layer Capacitance of Strongly Inverted Semiconductor Surfaces

Solid State Electronics 17, 377-385 (1974)

Supported by the National Science Foundation under Grants GH-33634 and GK-30283, and by AFOSR-71-2067

T. H. Ning and C. T. Sah

Effects of Inhomogeneities of Surface-Oxide Charges on the Electron Energy Levels in a Semiconductor Surface-Inversion Layer

Physical Review B9, 527-535 (1974)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10, by the National Science Foundation under Grant GH-33634, and by AFOSR-71-2067

C. T. Sah and H. S. Fu

Transient Response of MOS Capacitors Under Localized Photoexcitation

IEEE Trans ED-21, 202-209 (1974)

Supported by the Advanced Research Projects Agency under Contract LAHC-15-73-G10, by the National Science Foundation under Grants GH-33634 and GK-30283, and by AFOSR-71-2067

C. T. Sah and F. A. Lindholm

Transport in Semiconductors with Low Scattering Rate and at High Frequencies
Solid State Electronics 16, 1447 (1973)

Supported by the National Science Foundation under Grant GH-33634, by
the Advanced Research Projects Agency under Contract HC-15-67-C-0221,
and by AFOSR-71-2067

C. T. Smiley, L. D. Yau, and C. T. Sah

Application of the Transmission Line Equivalent Circuit Model to the Analysis
of the pn Junction Admittance Under dc Bias

Solid State Electronics 16, 895-901 (1973)

Supported by the Advanced Research Projects Agency under Contract
HC-15-67-C-0221, by the National Science Foundation under Grant GK-30283,
and by AFOSR-71-2067

J. W. Walker and C. T. Sah

Spherical-Square-Well Defect-Potential Model for 1-MeV Electron Irradiated
Defects in Silicon

Physical Review B 8, 5597-5603 (1973)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grant GH-33634,
and by AFOSR-71-2067

J. W. Walker and C. T. Sah

Characteristics of 1.0 MeV Electron-Irradiated Surface-Controlled Silicon
Junction Diodes

Radiation Effects 20, 187-195 (1973)

Supported by the Advanced Research Projects Agency under Contract
HC-15-67-C-0221 and by AFOSR-71-2067

L. D. Yau and C. T. Sah

Quench-in Centers in Silicon p^+n Junctions

Solid State Electronics 17, 193-201 (1974)

Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10, by the National Science Foundation under Grant GH-33634,
and by AFOSR-71-2067

F. Hennig and C. T. Sah

Matrix Analysis of Distributed Semiconductor Circuit Models

Solid State Electronics 16, 1081-1083 (1973)

Supported by the National Science Foundation under Grant GK-30283

Sokrates T. Pantelides and C. T. Sah

Theory of Localized States in Semiconductors. I. New Results Using an Old Method

Physical Review (submitted to)

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10, by the National Science Foundation under Grant GH-33634, and by AFOSR-71-2067

Sokrates T. Pantelides and C. T. Sah

Theory of Localized States in Semiconductors. II. The Pseudo Impurity Theory Application to Shallow and Deep Donors in Silicon

Physical Review (submitted to)

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10, by the National Science Foundation under Grant GH-33634, and by AFOSR-71-2067

M. J. McNutt and C. T. Sah

The Effects of Spatially Inhomogeneous Oxide Charge Distribution on the MOS Capacitance-Voltage Characteristics

Journal of Applied Physics (submitted to)

Supported by the Advanced Research Projects Agency under Contract

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M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

Sokrates Theodore Pantelides (C. T. Sah, Adviser)

Theory of Point-Imperfection States in Semiconductors

June 1973

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by AFOSR-71-2067, and by U. of I. Grad. Fellowship

Falke Hennig (C. T. Sah, Adviser)

Emission and Capture of Electrons and Holes at Gold Centers in Silicon at Thermal Equilibrium

May 1974

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10, by AFOSR-714-67, AFOSR-71-206, and by the National Science Foundation under Grants GH-33634 and GK-30283

Light Scattering from Disordered Materials

Principal Investigator: Miles V. Klein, Ph.D.
Professor of Physics

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Miles V. Klein, Professor
Wayne Wozniak, Research Associate
Valters Ziraps, Soviet Exchange Scholar (9/15/73-5/22/74)

Junior Staff: James E. Clemans, Research Assistant
Robert A. Field, Research Assistant and University Fellow
David Gallagher, Research Assistant
John A. Holy, Research Assistant

Objectives: To study light-scattering from hydrogen diffusing and vibrating in metals such as niobium (with H. K. Birnbaum). To perform similar measurements on inorganic salts containing rapidly diffusing ions. To study light scattering in glasses with emphasis on temperature-dependence of the Brillouin linewidth and on residual depolarized Rayleigh scattering. To study the infrared and Raman vibrations in organic charge-transfer complexes, especially those that show high conductivity.

Approach: Use of a double grating Raman spectrometer and single and triple-passed Fabry-Perot interferometer for the measurements of scattered-light spectra. Development of a special high-vacuum, controlled temperature, controlled atmosphere chamber for the metal samples. Obtain suitable crystals and sample mounts for temperature-dependent Raman studies above room temperature.

Progress: (01 07 73 - 30 06 74) The special chamber and samples are ready for the hydrogen-in-metals experiments. Some samples of highly conducting salts are being prepared. Both systems require special techniques to reject stray light. These are being developed.

The glass experiments require an extremely stable Fabry-Perot interferometer. This system with its related equipment is being assembled.

We have recently obtained low temperature Raman spectra for single crystals of the highly conducting charge transfer complex TTF-TCNQ. Although we can report no dramatic differences between the spectra at room temperature and liquid He temperature, other facets of the spectra indicate significant changes in the TCNQ species in forming the complex.

In addition, we have begun a normal coordinate analysis on TTF, the other organic member of the complex. Infrared and Raman spectra of KBr pellets of TTF have been obtained and we are in the process of using this data to study the normal vibrations of this molecule. The results of these calculations will be used in conjunction with the previous vibrational analyses of TCNQ in the interpretation of the spectra of TTF-TCNQ.

A program of study of second-order Raman scattering and of impurity induced Raman scattering from solidified gases was begun in collaboration with Professor R. K. Crawford. The gases are solidified at high pressures to allow study of the density dependence of the scattering and to facilitate handling of these normally fragile specimens. Preliminary data have been obtained for the temperature and density dependences of the second order scattering from pure solid argon and for the impurity induced scattering from argon doped with krypton. Various other combinations of host material and impurities are contemplated.

Point defects produced by x-irradiation of KBr crystals at 5.2 K and recombination phenomena have been studied by simultaneous measurement of thermally

stimulated currents (TSC) and depolarization currents (TCDS), optical absorption charges and non-isothermal bleaching curves. One goal was to determine the electrical charge state of the primary Frenkel defects produced by the x-irradiation, i.e. does the annihilation of radiation-produced electron-hole pairs or excitons cause charged (α -I) or neutral (F-H) primary disorder? Present results confirm earlier high temperature results that favor the charged-primary-defect processes.

Publications: (01 07 73 - 30 06 74)

B. N. Ganguly

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Physical Review B8, 1055-1060 (1973)

Supported by the National Science Foundation under Grant GH-33634

B. N. Ganguly

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Zeitschrift für Physik 265, 433-439 (1973)

Supported by the National Science Foundation under Grant GH-33634

B. N. Ganguly

The Gruneisen Constant for Hydrogen Mode in PdH System
Physics Letters 46A, 23-24 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grant GH-33634

Miles V. Klein

The Equivalence of Resonance Raman Scattering in Solids with Absorption Followed by Luminescence

Physical Review-Comments and Addenda 8, 919-921 (1973)

Supported by the National Science Foundation under Grants GH-33634 and GP-28319

Judith G. Peascoe and Miles V. Klein

Raman Scattering by the Hydroxyl Ion in Sodium Chloride
Journal of Chemical Physics 59, 2394-2408 (1973)

Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10 and by the National Science Foundation under Grants GP-11173 and GP-28319

Judith G. Peascoe, W. R. Fenner, and Miles V. Klein

Raman Scattering by the Hydroxyl Ion in KCl and KBr

Journal of Chemical Physics (submitted to)

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under Grants GH-33634, GH-37757, GP-11173, and GP-28319

M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

None

Light Scattering in Solutions of Polymers, Macromolecules, Dense Gases
Liquids, and Liquid Crystals

Principal Investigator: Willis H. Flygare, Ph.D.
Professor of Chemistry

Supporting Agency: Advanced Research Projects Agency

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Junior Staff: Sidney Bertucci, Research Assistant
Alan Burnham, Teaching Assistant
Timothy D. Gierke, Research Assistant
Steve Hartford, NSF Trainee
Yoshiaka Ishizu, Japanese National (Term 5/20/74)
Tilak Raj, Biophysical Trainee

Objectives: The general objectives are to study the interactions of molecules in dense gases, liquids, liquid crystals, and solutions. We are interested in the forces of interaction and dynamics between molecules and atoms in liquids and solids. In addition, we are interested in the hydrodynamic properties of macromolecules and polymers in solution.

Approach: The primary approach in our study is to analyze the frequency spectrum and intensities of light scattering from the various systems described above. The spectrum of the light contains information about the dynamics of motion in the scattering systems. The intensities obtained from the integrated spectrum gives information about the static correlations in the system. We are studying both positional and orientational static and dynamic correlations.

Progress: (01 07 73 - 30 06 74) We have made significant progress during this last year in studying the orientational pair correlations in several liquid crystal-like systems. By studying the spectrum of the depolarized

light in the isotropic liquid phase of liquid crystal-like molecules (and the dilution dependence in carbon tetrachloride) we can relate the onset of liquid crystal phase to a critical density. This work is being continued in a wide range of liquid crystal-like molecules in order to understand the nature of the attractive forces in liquid crystal systems. We have also made progress in understanding the nature and the effects of the nonspherical Lorentz correction to the intensity of the scattered light in binary systems.

Publications: (01 07 73 - 30 06 74)

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Annual Review of Materials Science 4 (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

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Applied Optics 12, 2838-2844 (1973)
Supported by the National Science Foundation under Grant GH-33634

J. C. McGurk, T. G. Schmalz, and W. H. Flygare
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Advanced Chemical Physics XX, Edited by I. Prigogine and S. A. Rice, (John Wiley and Sons, 1974)
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W. H. Flygare and R. A. Huggins
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Journal of Chemical Physics 59, 1796-1805 (1973)
Supported by the National Science Foundation (Non-MRL)

J. C. McGurk and W. H. Flygare

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C. L. Norris, E. F. Pearson, and W. H. Flygare

The Molecular Zeeman Effect in Methyl Fluoride
Journal of Chemical Physics 60, 1758-1761 (1974)

Supported by the National Science Foundation (Non-MRL)

E. F. Pearson, C. L. Norris, and W. H. Flygare

Molecular Zeeman Effect, Electric Dipole Moment, and Boron Nuclear Hyperfine
Coupling Constants in HBS

Journal of Chemical Physics 60, 1761-1770 (1974)

Supported by the National Science Foundation (Non-MRL)

S. L. Rock, E. F. Pearson, E. Appleman, C. L. Norris, and W. H. Flygare

The Molecular Rotational Zeeman Effect in HOF, a Comparison with H₂O
F₂O₁ and other Fluorine Containing Molecules; and Dipole Moments of HOF
and DOF

Journal of Chemical Physics 59, 3940-3947 (1973)

Supported by the National Science Foundation (Non-MRL)

T. G. Schmalz, C. L. Norris, and W. H. Flygare

Localized Magnetic Susceptibility Anisotropies

Journal of the American Chemical Society 95, 7961-7974 (1973)

Supported by the National Science Foundation (Non-MRL)

W. H. Flygare

Magnetic Interactions and the Electronic Structure of Diamagnetic Molecules

Advances in Chemistry, Critical Evaluation of Chemical and Physical Structural
Information, Edited by D. R. Lide and C. K. Johnson, 1974

Supported by the National Science Foundation (Non-MRL)

J. L. McGurk, C. L. Norris, T. G. Schmalz, E. F. Pearson, and W. H. Flygare

Infrared-Microwave Double Resonance Measurements of T₁ in Methyl Fluoride
and Methyl Chloride

Proceedings of the First International Symposium of Laser Spectroscopy,
1973, Edited by A. Moradian and R. Brewer

Supported by the National Science Foundation (Non-MRL)

T. D. Gierke and W. H. Flygare

Depolarized Raleigh Scattering in Liquids: Molecular Reorientation and
Orientation Pair Correlations in a Nematic Liquid Crystal: MBBA

Journal of Chemical Physics (submitted to)

Supported by the Advanced Research Projects Agency under Contract

DAHC-15-73-G10

J. C. McGurk, T. G. Schmalz, and W. H. Flygare
Fast Passage in Rotational Spectroscopy: Theory and Experiment
Journal of Chemical Physics (submitted to)
Supported by the Advanced Research Projects Agency under Contract
DAHC-15-73-G10

W. H. Flygare and B. R. Ware
Analysis of Polymer Mixtures in Solution Utilizing Electrophoretic Light
Scattering Apparatus
United States Patent No. 3,766,048, October 16, 1973

M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

C. L. Norris (W. H. Flygare, Adviser)
Molecular Zeeman Effect Studies and Time Resolved Infrared-Microwave
Double Resonance
August 1973
Non-MRL Supported

High-Pressure Nuclear Magnetic Resonance and Raman Study of the Dynamic Structure of Liquids, Disordered Solids and Polymers

Principal Investigator: Jiri Jonas, Ph.D.
Professor of Chemistry

Supporting Agency: Advanced Research Projects Agency

Senior Staff: Jiri Jonas, Professor

Junior Staff: John H. Campbell, Research Assistant
Yun-Ko Lee, Research Assistant (Term 10/10/73)
Hugh J. Parkhurst, Research Assistant
David J. Wilbur, Research Assistant

Objectives: The general aim of the research is to improve our understanding of the dynamic structure of liquids, disordered solids and polymers by investigation of motions and interactions at the molecular level. In a systematic way we attempt to obtain experimental data which will enable us to draw conclusions of general validity about the reorientation mechanism and transport properties of liquids. In the area of disordered solids the main interest is in the nature of the order-disorder transitions and the hysteresis effects accompanying such transitions. Preliminary studies of elastomers are directed towards elucidation of the relationship between the dynamic structure and the mechanical properties of polymers.

Approach: The most important feature in all our experiments is that we use both pressure and temperature as experimental variables which enables us to separate the effects of density and temperature on the dynamic processes studied. In particular the constant density experiments are important as a means to obtain information about the true effect of temperature on the dynamic process. Several experimental techniques are used to investigate

the molecular motions and interactions in the materials of interest:

(1) Nuclear magnetic resonance spin-lattice relaxation times are measured over a wide range of temperatures and pressures. (2) The NMR spin echo method using the fixed magnetic field gradient is employed to determine diffusion coefficients. (3) Fourier transform deconvolution technique is used to obtain the time dependence of reorientational and vibrational correlation functions from laser Raman band shapes. (4) Shear viscosities and PVT data are also studied in liquids.

Progress: (01 07 73 - 30 06 74) (1) Both Raman and NMR techniques were used in a detailed investigation of the molecular motions of a symmetric-top molecule methyl iodide- d_3 in the liquid state. The method of Fourier transform deconvolution was used to obtain the correlation functions from the Raman spectra. For the first time it was possible to separate the effects of density and temperature on the reorientational correlation functions and the vibrational correlation functions. All results show the dominant effect of density on molecular motions. On the basis of this study, we concluded that the model of a hard sphere liquid, the assumption of binary collisions and the temperature dependence of the hard sphere diameter appear to be promising concepts leading to a better description of the liquid state.

(2) NMR studies of spin rotation interaction relaxation mechanism provide unique information about the angular momentum in liquids. One determines the angular momentum correlation time, τ_J , which corresponds to the time it takes the molecule to lose memory of its initial angular momentum. There are two important results of our studies. First, the Gordon J-diffusion model

describes well the reorientation of molecules not only in dense fluids but also at supercritical temperatures and becomes equivalent to a perturbed free rotor model in the dilute gas limit. Secondly, for the first time, we were able to follow the temperature behavior of τ_J at constant density and found that experimental τ_J increases with increasing temperature at constant density. This finding is of particular interest because τ_J is related to the time between collisions. We interpreted the experimental data in terms of the Enskog theory and the cell model which were used to calculate the theoretical time between collisions (τ_{BC}). In order to obtain the correct prediction of the observed temperature change in τ_J ($\propto \tau_{BC}$) at constant density we had to assume a temperature dependence of the hard sphere diameter.

(3) As a part of our systematic effort to elucidate some of the problems of the dynamic structure of electrolyte solutions, we have finished a study of the effects of pressure and temperature on the dynamic structure of several electrolyte solutions. Both structure breaking and structure forming ions were investigated. The determination of motional behavior of water molecules in solvation shells of the ions was possible.

(4) The first results of our experiments on NMR relaxation in disordered solids show convincingly that these studies will be fruitful in investigating order-disorder transitions and the hysteresis effects accompanying such transitions. By following the effect of temperature and pressure on relaxation in several polymers, e.g., we determined the pressure dependence of the glass transition temperature which information is of theoretical and practical interest.

(5) New experimental NMR setup, which enables us to measure the spin lattice relaxation times and diffusion coefficients at pressures up to 10 kbar and temperatures up to 300°C was built and tested. Measurements of heavy water and various electrolytic solutions are in progress.

Publications: (01 07 73 - 30 06 74)

J. Hyde Campbell, J. F. Fisher, and J. Jonas
Density and Temperature Effects on the Molecular Reorientation and Vibrational Relaxation in Liquid Methyl Iodide
Journal of Chemical Physics 60, (1974)
Supported by the Advanced Research Projects Agency under Contract DAHC-15-73-G10

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Reorientational and Angular Momentum Correlation Times in Gaseous Tetrafluoromethane at Moderate Densities
Journal of Chemical Physics 59, 4151-4156 (1973)
Supported by the National Science Foundation under Grants GH-33634 and GP28268X

J. Jonas
NMR Relaxation in Liquids and Liquid Crystals
Magnetic Resonance Review 2, 203-220 (1973)
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J. Jonas
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Advances Magnetic Resonance 6, 73-139 (1973)
Supported by the National Science Foundation under Grant GH-33634 and by the Advanced Research Projects Agency under Contract HC-15-67-C-0221

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Journal of Chemical Physics 60, 3223-3245 (1974)
Supported by the USAFOSR under Contract AF-72-2286

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Journal of Physical Chemistry 77, 1768-1772 (1973)
Supported by the National Science Foundation under Grant GP-28268X and by the USAFOSR under Contract AF-72-2286

J. Jonas, J. DeZwaan, and J. H. Campbell
Nuclear Magnetic Resonance Relaxation Studies of Reorientational Motions in Liquids at High Pressure
Proceedings of Conference (J. Lascombe, Ed., D. Riedel Publishing Co., Dordrecht, Holland, 1974) pp. 343-353
Supported by the National Science Foundation under Grant GP-28268X and by the USAFOSR under Contract AF-72-2286

M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

Yun Ko Lee (J. Jonas, Adviser)
High Pressure Nuclear Magnetic Resonance Studies of Hydrogen - Bonded Systems
January 1974
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Liquid Crystals and Phase Transitions

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Supporting Agency: Advanced Research Projects Agency

Senior Staff: William McMillan, Professor

Junior Staff: Ravindra Bhatt, Research Assistant and University Fellow
Kung Chao Chu, Research Assistant
Chung-Shih Hsu, Research Assistant
Robert J. Meyer, Research Assistant
Mark P. Sears, Research Assistant

Objectives: We want to produce physical theories of the various liquid crystal phases and to subject the theories to rigorous experimental tests. The objective, broadly speaking, is to advance liquid crystal physics from its present rather primitive state to the advanced level of solid state physics.

Approach: Three theoretical approaches are being pursued vigorously:

(1) Microscopic theory based on a model intermolecular interaction treated within the mean field approximation; (2) Phenomenological (Landau) theories based on the order parameter dependence of the free energy. Both static and dynamic theories are possible; (3) Wilson theory of the critical behavior near a second order phase transition. The experimental approach being pursued at present is light scattering using the self-beating technique. Light scattering provides an experimental probe of the static and dynamic behavior of the liquid crystal director. Several theories of the second order smectic A-nematic phase transition are now available to be tested.

Progress: (01 07 73 - 30 06 74) (1) A microscopic theory of the smectic C, B, and H phases is completed. The theoretical results include a phase diagram for the smectic phases as well as predictions of the temperature dependence

of thermodynamic properties and order parameters.

(2) We are currently trying to construct a microscopic model of the two new phases of TBBA.

(3) A dynamic Landau theory of the smectic A-nematic phase transition has been constructed to explain the pretransition increase in the nematic viscosity coefficients recently observed.

(4) We are struggling with the problem of producing a dynamical theory in the critical region analogous to the static Wilson theory.

(5) The light scattering apparatus and an elaborate hot stage (with temperature control within ± 1 mK) have been constructed and tested. We are now learning to purify and control the liquid crystals so that measurements of elastic constants and viscosities can be made within a few millikelvin of the phase transition. This experiment will provide a rigorous test of the static and dynamic behavior of nematics near the transition to the smectic A phase.

The following two problems are only loosely related to the liquid crystal effort.

(6) We have found a new way Wilson theory. This is quantification of Kadanoff's block spin concept and we have developed the ideas by applying them to a calculation of the critical behavior of the two-dimensional Ising model.

(7) A theory of anomalous dispersion in liquid He^4 has been developed to explain propagation of high frequency phonons recently observed by Dynes and Naharanamurti.

Publications: (01 07 73 - 30 06 74)

W. L. McMillan

A Simple Molecular Theory of the Smectic C Phase

Physical Review A₈, 1921-1929 (1973)

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W. L. McMillan

Time Dependent Landau Theory for the Smectic A-Nematic Phase Transition

Physical Review A₉, 1720-1724 (1974)

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W. L. McMillan

Molecular Order and Molecular Theories of Liquid Crystals

American Chemical Society Symposium on Ordered Fluids and Liquid Crystals
Chicago, 1973 (submitted to)

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M. S. Thesis: (01 07 73 - 30 06 74)

None

Ph.D. Thesis: (01 07 73 - 30 06 74)

None